



Short communication

Study of reactions of activated Mg-based powders in heated steam



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H I G H L I G H T S

- The activated Mg-based powders were prepared by high-energy ball milling.
- The reactivity of Mg-based powders in heated steam was effectively improved.
- Co_3O_4 plays an important role for the activated Mg-based powders.
- Mg-based powders with flowing steam oxidized at 500 °C, and ignited at 600 °C.

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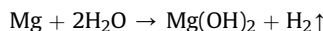
A B S T R A C T

Activated Mg-based powders are prepared by high-energy milling and characterised with XRD, SEM, TG and BET techniques. This study focus on reactions of Mg-based powders with flowing steam that is heated at 500, 600, and 700 °C in a transparent pipe furnace. Morphologies and phases of solid reaction products are analysed by SEM, XRD, and residual metal content, and ignition delay times are measured. Experimental results show that all Mg-based powders oxidise at 500 °C and ignite at 600 °C. At 700 °C, all samples burn completely to form magnesium oxide (MgO) within 5 min. Residual metal contents and ignition delay times of all samples decrease with increasing temperature, and ignition delay times of activated Mg-based materials containing cobalto-cobaltic oxide (Co_3O_4) are only 22 s at 700 °C. Milled Mg powders are more reactive in heated steam than unmilled Mg powders, and the addition of Co_3O_4 further increases magnesium reactivity in heated steam.

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1. Introduction

Because reactions between metals and water result in high energy densities and can produce large amounts of hydrogen, these reactions are under consideration for underwater power generation and hydrogen production applications [1]. A combination of solid powdered magnesium as fuel and water as oxidising agent may be an interesting green underwater propellant system. The reaction between magnesium and water is as follows:



$$\Delta H_r = -354 \text{ KJ mol}^{-1}$$

In this reaction, the hydrogen yield is 3.3 wt% (including the mass of water) or 8.2 wt% (without including water in the calculation). In addition to producing relatively large amounts of energy

and hydrogen, this reaction is also desirable because the oxidising agent (water) is readily available and easy to store, and Mg powder is relatively inexpensive and its oxidation products (magnesium oxide or hydroxide) are environmentally friendly. Therefore, in recent years, Mg/ H_2O combustion has been studied for producing energy for underwater propulsion systems.

Many recent studies have focused on fundamental characteristics of metal/water reactions [2–7]. On one hand, certain studies investigate reactions of original metals with water: T.F. Miller [8] developed a finite rate kinetic model of Mg particle/water vapour reactions and applied it in a numerical study of combustion. T.W. Megli et al. [9] studied the ignition of Al/Mg alloys in water vapour and argon and conducted experiments on reaction kinetics of Al/Mg alloys with water vapour. Other authors performed experimental investigations on diffusion dominated burning rates of Mg particles in water vapour [10,11]. V.V. Gorbunov [12] studied combustion reactions of high-calorific metal powders and water and determined that combustion performance depended primarily on the degree of oxidation of metal powder. On the other hand, some studies focus on the activation of Mg powders for hydrogen production at normal temperatures. Several methods [1,13–17],

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such as ball milling, the preparation of fine magnesium dispersions, and the use of catalysts, have been developed for the mechanical and chemical activation of magnesium. M.S. Zou et al. [1,18] reported that Mg-based hydro-reactive materials including Co, Ni and Bi were more reactive in seawater than milled Mg powder due to the creation of micro-galvanic cells. M.H. Grosjean et al. [17] reported that hydrolysis kinetics and yields were maximised for Mg-10 wt% Ni composites milled for 30 min, and the reaction of this composite with water was complete within an hour in the presence of chloride ions. According to Ouyang et al. [19], a Mg–La system was prepared and underwent controlled reactions at room temperature without addition of a catalyst, and the reaction mechanism of hydrogenated Mg_3La was consistent with a three-dimensional interface reaction process. Alloys of magnesium with aluminium, lithium, mercury, platinum, and other metals have also been considered [20–23].

The above analysis find that the researchers tend to be more focused on the combustion performance of the original metal with water and the activation of the Mg-based powders with water at ambient temperature. However, no experimental studies on reactions of activated Mg-based powders with steam heated at high temperatures were reported. Therefore, this study was undertaken to study reactions of Mg-based powders with heated steam fed through a transparent pipe furnace. The objective of this paper is to study an efficient method and addition for improving the reactivity of Mg-based powders in heated steam at high temperatures. The results of this study will provide a theoretical basis for applications of activated Mg-based powders in a power system based on the metal-fuelled heat engines.

2. Experimental

2.1. Sample preparation

We prepared three samples of Mg-based powders with the compositions shown in Table 1.

The starting materials were elemental magnesium (Mg, 99.8 wt %, –325 mesh) and cobalto-cobaltic oxide (Co_3O_4 , 99.9 wt%) powders. This magnesium was produced by the Weihao Company of China. Cobalto-cobaltic oxide powders were analytical grade chemicals. Milling experiments were performed in a ball mill (Simoloyer CM01) under argon to prevent oxidation. The process parameters for milling are shown in Table 2.

2.2. Sample characterisation

Scanning electron microscopy (SEM) observations were made using a TM 3000 microscope.

The fresh metal content of each powder was measured volumetrically. This method measured the volume of hydrogen produced by the reaction of a powder sample with HCl solution. A schematic diagram of the apparatus is shown in Fig. 1.

Samples were characterised by X-ray diffraction (XRD) using an X'Pert PRO MPD diffractometer with $\text{Cu-K}\alpha$ radiation.

Table 1
Composition of Mg-based materials.

Sample	Mg wt%	Co_3O_4 wt%	Milling time/h
Mg-1	100		0
Mg-2	100		1
Mg-3	98	2	1

Table 2
Milling equipment and process parameters.

Ball mill	Simoloyer CM01-21
Milling balls	Material: steel (100Cr6), diameter: 5.1 mm
Powder/ball mass ratio	1:10
Milling atmosphere	Argon
Milling time	1 h
Rotating speed	1200 rpm (48 s), 800 rpm (12 s)
Operating mode	Cyclic
Cooling-grinding system	Water

Specific surface areas of samples were measured with the BET method (low temperature adsorption of nitrogen).

The powder median diameters (D50) were determined using a Laser Particle Size Analyzer MS 2000.

Thermogravimetric (TG) analysis was performed with a NETZSCH F209 apparatus, at 40–950 °C in air at a flow rate of 30 mL min^{−1} and a heating rate of 10 °C min^{−1}.

Reactions of Mg-based powders in heated steam were performed in the experimental apparatus shown in Fig. 2. Samples (~0.5 g, measured accurately) were placed in an alumina crucible, which was put in a transparent pipe furnace where the temperature was controlled with a thermoregulator. Steam was fed into the pipe at 500, 600, or 700 °C for 5 min. Solid combustion products were collected and their fresh metal contents were measured.

3. Results and discussion

3.1. Characterisation of Mg-based powders

3.1.1. Properties of Mg-based powders

As shown in Table 3, specific surface area S_{sp} , D50 and bulk density of Mg-2 decreased relative to Mg-1, which was due to metal powder aggregation during ball milling. In contrast, S_{sp} of Mg-3 powder increased significantly and D50 decreased, which reflected the influence of the Co_3O_4 additive. During ball milling, Co_3O_4 acts as a process control agent that prevents clean Mg-to-Mg contacts that are necessary for cold welding, and thus, Co_3O_4 promotes powder fracture [24]. The fresh metal contents of Mg-2 and Mg-3 indicated that no significant Mg oxidation occurred during the 1 h milling process under inert argon atmosphere.

3.1.2. Particle morphology

Scanning electron microscopy (SEM) images of powders are shown in Fig. 3. Particles of Mg-1 powders were regular spheres. When Mg powders were milled for 1 h, spherical particles were replaced by irregularly shaped larger particles. With the addition of

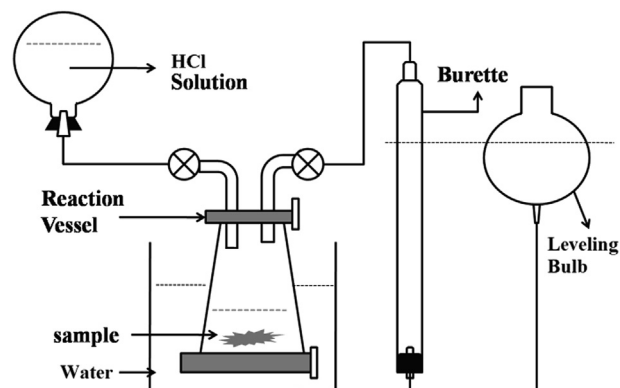


Fig. 1. Schematic diagram of the apparatus used to measure fresh metal content in powder samples.

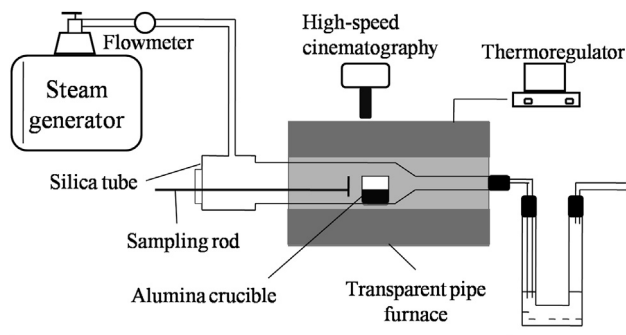


Fig. 2. Schematic diagram of the apparatus used to observe reactions in heated steam.

Table 3
Properties of Mg-based powders.

Sample	Specific surface area (S_{sp}) (BET) $\text{m}^2 \text{g}^{-1}$	D50, μm	Fresh Mg content, wt%	Bulk density, g cm^{-3}
Mg-1	1.04	76.15	99.8	0.89
Mg-2	0.77	97.23	99.1	0.75
Mg-3	4.76	58.35	96.9	0.52

Co_3O_4 , Mg-3 powders formed flake-like structures with a very broad size distribution. Particles of Co_3O_4 are clearly visible and dispersed homogeneously in the powders.

3.1.3. Phase structures

Fig. 4 shows XRD spectra of Mg-1, Mg-2, and Mg-3 powders. Magnesium peaks are clearly present in the spectrum for Mg-1 powder. In the case of Mg-2 powder, milling caused no major structural modifications in the spectrum, but milling accentuated peak broadening due to smaller Mg crystallites [17]. An increase in Mg (0 0 2) relative peak intensity at 34.4° is observed for Mg-2 and Mg-3 powders, indicating preferential orientation along the *c*-axis. This preferential orientation may occur because less energy is required for slip deformation perpendicular to the *c*-axis than for deformations in other directions [16]. Peaks attributed to Co_3O_4 phases are discernible in the Mg-3 spectrum, but these peaks are very weak due to low Co_3O_4 content.

3.2. Reaction of Mg-based materials with heated steam

Solid products were collected after Mg-1, Mg-2, and Mg-3 powders reacted with steam heated at 500, 600, or 700 °C for

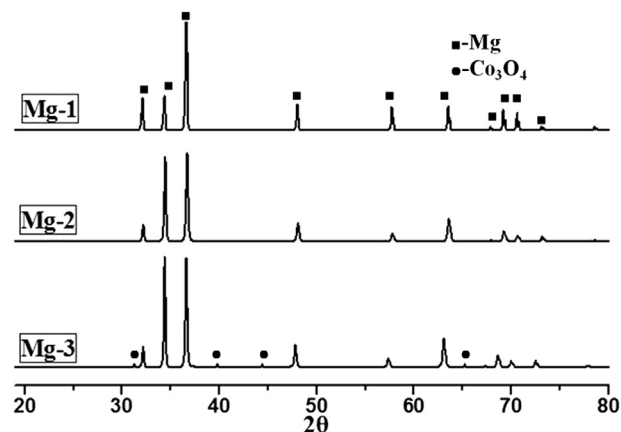


Fig. 4. XRD spectra of the Mg-1, 2, 3.

5 min. Residual fresh metal contents of reaction products were measured using the experimental apparatus shown in Fig. 1. Product phases were characterised by X-ray diffraction (XRD), and ignition delay times were measured with a timer. These results are shown in Table 4.

It was immediately apparent when Mg-based materials reacted with heated steam. At 500 °C, XRD data showed that these three samples did not ignite and only oxidised to form $\text{Mg}(\text{OH})_2$ in 5 min. The extent of oxidation for Mg-1, Mg-2, and Mg-3 was 7.5, 14.5, and 24.1 wt%, respectively. At 600 °C, every sample ignited and burned in the heated steam, and the ignition delay time decreased from Mg-1 to Mg-3. The XRD results for these Mg-containing products indicated that the samples did not react completely in 5 min. When the temperature reached 700 °C, all samples reacted completely to form MgO. The addition of Co_3O_4 decreased ignition delay times to 22 s, it is over 100 s shorter than ignition delay times for Mg-1 and Mg-2.

We concluded that milled samples were more reactive than unmilled samples and Co_3O_4 addition further improved reactivity of milled Mg powders. According to Skrovan et al. [25], ball milling processes are very promising for activation of Mg powders due to the elimination of oxide layers and creating surface defects. Addition of Co_3O_4 produces a constituted low-overvoltage cathode, which facilitates hydrogen evolution at a substantial corrosion rate [26].

Morphology changes during reactions at different temperatures were studied by SEM, Fig. 5. At 500 °C, oxidation of Mg-1 started at powder particle surfaces with the formation of rough surfaces. As the temperature increased to 600 °C, some Mg-1 powder particles

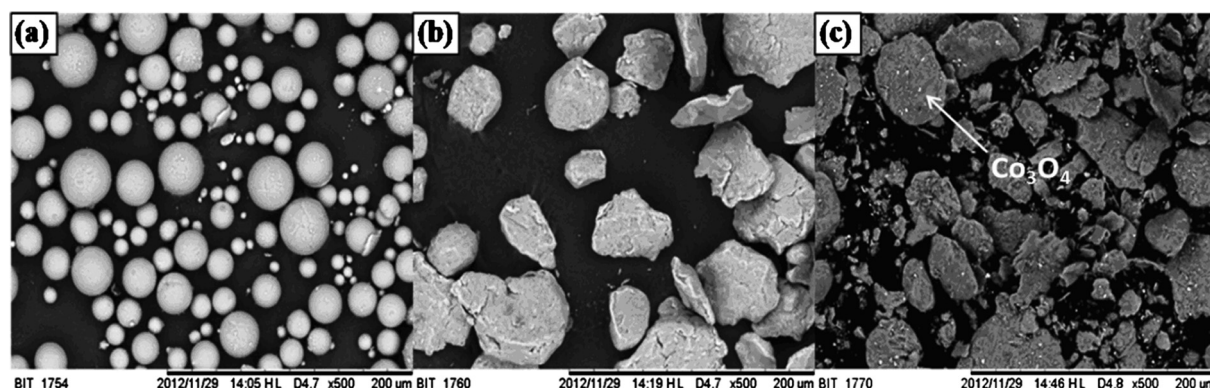


Fig. 3. SEM micrographs of (a) Mg-1, (b) Mg-2, and (c) Mg-3.

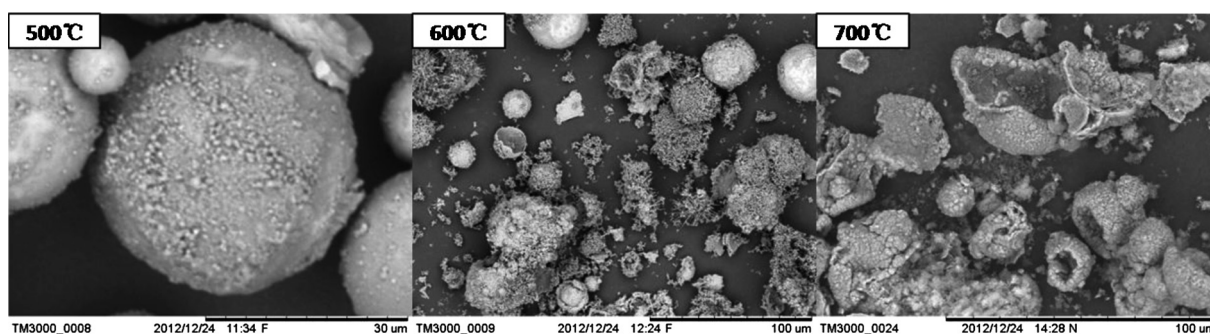
Table 4

Results for fresh metal content, magnesium phase, and ignition delay time for original samples and products from reactions with steam at three temperatures.

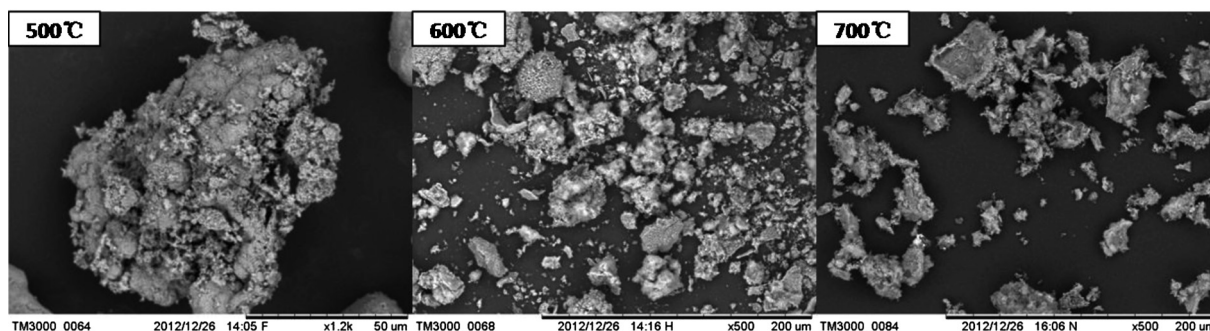
		Original sample	500 °C steam	600 °C steam	700 °C steam
Mg-1	Fresh Mg content, wt%	99.8	92.5	24.0	0
	Phase	Mg	Mg, Mg(OH) ₂	Mg, MgO	MgO
	Ignition delay time, s	—	—	277	146
Mg-2	Fresh Mg content, wt%	99.1	84.6	9.4	0
	Phase	Mg	Mg, Mg(OH) ₂	Mg, MgO	MgO
	Ignition delay time, s	—	—	254	134
Mg-3	Fresh Mg content, wt%	96.9	72.8	6.8	0
	Phase	Mg	Mg, Mg(OH) ₂	Mg, MgO	MgO
	Ignition delay time, s	—	—	186	22

broke apart. When the temperature increased further, product structure became varied and laminated. For milled powders (Mg-2 and Mg-3), oxidation also started at powder particle surfaces at 500 °C, but products formed smaller, irregularly shaped flakes as the temperature increased to 600 °C. Particle sizes decreased further as the temperature reached 700 °C.

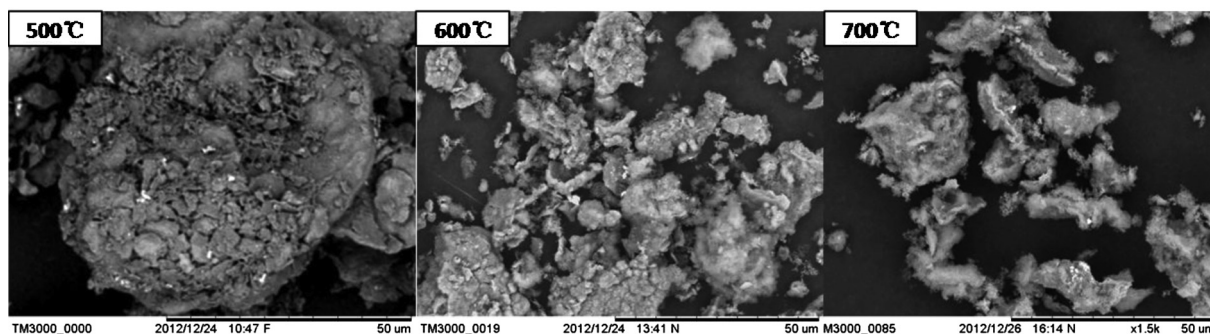
To further study the behaviour of these Mg-based powders, TG was used to measure their reactivity in air (Fig. 6). All three metal powders reacted with air to a significant extent, and TG traces for Mg-1, Mg-2, and Mg-3 showed sharp weight increases of 66.4, 65.1, and 62.2 wt%, respectively, in the range of 450–650 °C, which originates from the normal oxidation of Mg. As expected, Mg-2 and Mg-3 were substantially more reactive than Mg-1. Interestingly, oxidation onset temperatures differed for milled Mg and unmilled Mg powders. Comparing three samples that underwent a 5 wt% increase, oxidation started at lower temperatures for milled than unmilled samples, which was due to formation of fresh, chemically active metal surfaces by milling. The initial oxidation temperature of Mg-3 powders at approximately 420 °C was much lower than the



(a) SEM images of reaction products of Mg-1 powders



(b) SEM images of reaction products of Mg-2 powders



(c) SEM images of reaction products of Mg-3 powders

Fig. 5. SEM images of products from reactions of Mg-1, Mg-2, and Mg-3 with steam heated at 500, 600, and 700 °C.

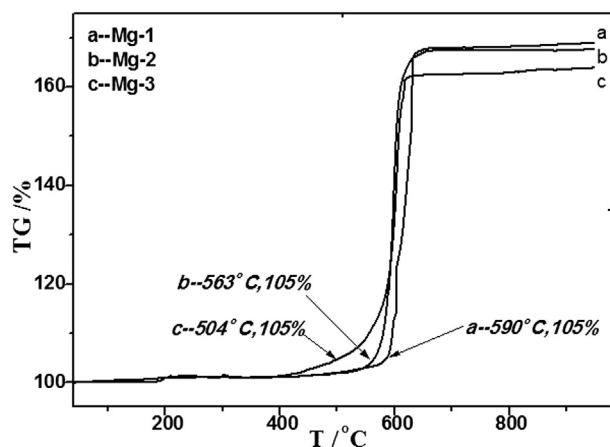


Fig. 6. TG traces for Mg-1, Mg-2, and Mg-3 powders.

initial oxidation temperature for Mg-2 powders. Milled powders were more active in air than unmilled powders, and Mg powders with added Co_3O_4 were the most reactive. This reactivity trend in air was in good agreement with the sample reactivity trend in heated steam.

4. Conclusions

This study focused on reactions of Mg-based powders with flowing steam at various high temperatures in a transparent pipe furnace. We activated Mg-based powders by high-energy ball milling, which accelerated Mg reactions with heated steam. The outcomes of this study are as follows:

- (1) High-energy ball milling of pure magnesium had a significant effect on Mg reactivity in heated steam, which was due to formation of fresh, chemically active metal surfaces and numerous defects.
- (2) During ball milling, addition of Co_3O_4 to Mg powders decreased $d(0.5)$ and increased specific surface area. Furthermore, Co_3O_4 shortened ignition delay times for Mg powders in heated steam and significantly accelerated Mg powder reaction rates compared to pure Mg milled powders. Measured TG traces

indicated similar sample reactivity trends in air and heated steam.

Acknowledgements

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